Disproportionation of HOD in Condensed Phases

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Summary The law of the geometric mean for the vapour pressure isotope effect in the series HOH, HOD, and DOD is not obeyed; rather $\ln[P(H_2O)/P(D_2O)]/\ln[P(H_2O)/P(HOD)] = 1{\cdot}91 \pm 0{\cdot}03$, so the equilibrium constant for the reaction HOH + DOD = 2 HOD, K_1 (condensed), is significantly larger than K_1 (dilute gas); the difference varies from 1·5 ± 0·5% at −25 °C to 0·3 ± 0·1% at 75 °C.

THE importance of a proper treatment of the equilibrium between HOH, DOD, and HOD in the treatment of solvent isotope effects has been pointed out by Gold[1] and Gold and Tomlinson,[2] among others. Recent[3,4] mass-spectrometric determinations of the gas-phase equilibrium constant as a function of temperature give results for K_1 (gas) between 3·74 ± 0·02 (at 0 °C) and K_1 (gas) = 3·80 ± 0·02 (at 75 °C). Theoretical calculations (including properly evaluated anharmonic corrections[5,6]) give slightly higher results (3·82 at 0 °C to 3·89 at 75 °C). Gold and Tomlinson[2] measured K_1 in the liquid phase (20 °C) by an n.m.r. technique, finding K_1 (liquid) = 3·94 ± 0·12, barely within experimental agreement with previous indirect determinations.[7,8] They have also pointed out that the correction $\Delta K = K_1$ (condensed) − K_1 (gas) can be evaluated from vapour pressure data. We here make this evaluation from recent high precision vapour-pressure isotope effect measurements on HOH–DOD,[9] and HOH–HOD.[10]

Pupezin *et al.*[9] recently redetermined the isotope effect on vapour pressures for the H_2O–D_2O system between −60 and 100 °C, and over most of that range their results, expressed as $\ln R = \ln [P(\text{HOH})/P(\text{HOD})]$, agree to ±0·0003 unit, substantially higher precision (particularly below 30 °C) than previously obtained. Similarly Majoube,[10] with a mass spectrometric technique for the HOH–HOD system, obtained results with an uncertainty of ±0·001 unit in $\ln R' = \ln [P(\text{HOH})/P(\text{HOD})]$. Merlivat and Nief's[11] determination of R' below 0 °C gave an uncertainty which is probably somewhat greater than 0·001.[10,11] The law of the geometric mean[12] predicts that $\ln R/\ln R' = 2$. We have evaluated $r = 2{\cdot}00 - (\ln R/\ln R')$ from the various data just given. The results are given in Table 1.

TABLE 1

t/°C	−30	−20	−10	0	10	20	30	40	50	60	70	80	90	100
r(s)[a]	0·08	0·08	0·07	0·05										
Uncertainty	0·03	0·03	0·03	0·03										
r(liq)[b]				0·08	0·09	0·10	0·10	0·10	0·11	0·10	0·10	0·09	0·08	0·06
Uncertainty				0·02	0·02	0·03	0·03	0·04	0·04	0·05	0·05	0·06	0·07	0·08

[a] From refs. 9 and 11. [b] From refs. 9 and 10.

TABLE 2

t °C	−25	0	25	75
ΔK_1	$0{\cdot}05_7$ $\pm 0{\cdot}01_9$	$0{\cdot}03_6$ $\pm 0{\cdot}01_2$	$0{\cdot}02_6$ $\pm 0{\cdot}00_9$	$0{\cdot}01_3$ $\pm 0{\cdot}00_4$

Within experimental precision the effect is temperature independent and r may reasonably be taken as 0·09 ± 0·03. We feel that the error is conservatively set. It is simple to show that $\ln K$ (condensed) − $\ln K$ (gas) = $r \ln R'$ and to evaluate the corrections as in Table 2. This gives, for example, an experimental value at 20 °C for K (liquid) of 3·78 ± 0·03 (ref. 3) and a theoretical one of 3·87 ± ?, to be compared with Gold and Tomlinson's directly measured value 3·94 ± 0·12.[2] The evaluation depends on the assumption of unit activity coefficient for HOD dissolved in HOH. Van Hook[13] has shown that this assumption is consistent with the very precise freezing point data of LaMer and Baker.[14]

Finally, under the assumption that r does not change on freezing, measurements on the liquid-solid fractionation factor[15] [for HOH (solid) + HOD (liq) = HOH (liq) + HOD (solid)] may be used together with data from ref. 9 to obtain a value for r. We find r = 0·12 ± 0·07 by placing equal weights on the determinations from the different laboratories, in satisfactory agreement with the value employed above, r = 0·09 ± 0·03.

This research was supported by a grant from the National Science Foundation.

(*Received, 8th February* 1972; *Com.* 206.)

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